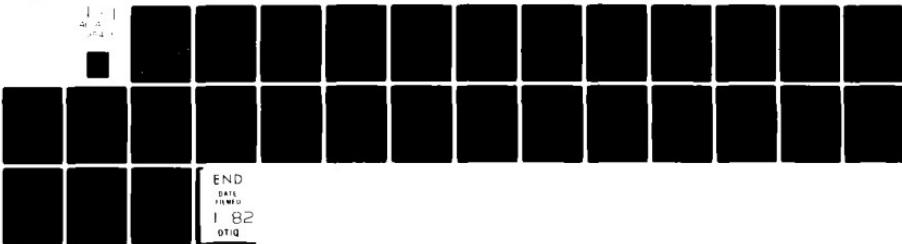
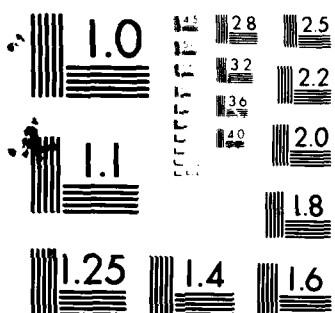


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Ab-Initio MODPOT/VRDDO/MERGE Calculations on Energetic Compounds

I. Mechanism of Initiation of Cationic Polymerization from
Electrostatic Molecular Potential Contour Maps*

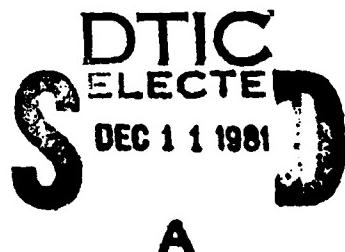
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Molecular and Solid State Theory, Palm Coast, Florida, March 1981. In
press International Journal of Quantum Chemistry, Symposium Issue.

*Paper XIII in the Series "Molecular Calculations With the Non-Empirical
Ab-Initio MODPOT/VRDDO/MERGE Procedures"

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ABSTRACT

Experimentally it had been observed in 1969 for cyclic ethers with conventional substituents that their propensity to polymerize was influenced by their basicities and ring strain. For energetic new polymers it was desired to predict the propensity to polymerize of cyclic ethers substituted with energetic groups prior even to synthesis of the monomers themselves. We carried out ab-initio quantum chemical calculations on these energetic cyclic ethers and generated the electrostatic molecular potential contour maps. These maps indicate vividly the basicities of the cyclic ethers and permit the relative ranking of their tendencies to polymerize. The maps also allow optimal choice of good copolymer candidates.

*Paper XIII in the Series "Molecular Calculations with the Non-Empirical Ab-Initio MODPOT/VRDDO/MERGE Procedures."

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I. Introduction

In support of an experimental study¹ concerned with the synthesis and polymerization of monomers of cyclic ethers substituted with exotic energetic groups such as nitro, fluoro, azido and azidomethyl we have carried out quantum chemical calculations designed to give insight on the following even prior to the synthesis of the monomers themselves.

- 1) Propensity of cyclic ethers to undergo cationic polymerization
- 2) What happens as a catalyst (a Lewis acid) approaches the cyclic ether monomer and what are the preferable catalysts.
- 3) What happens when a complex of cyclic ether plus catalyst approaches another molecule of cyclic ether monomer.
- 4) In some instances polymers derived from single monomers yield a product that is too refractory. In such an event what would be suitable and optimal reactants for co-polymerization to avoid this undesirable property.

*Paper XIII in the Series "Molecular Calculations With the Non-Empirical
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It had been observed by Japanese investigators² who studied experimentally three-to-six membered cyclic ethers with alkyl, alkoxy and aryl substituents that the rate of polymerization of cyclic ethers was proportional to

- a) the base strength of the cyclic ether
- b) the ring strain of the cyclic ether

Thus, to determine propensity for polymerization it was necessary to find theoretical indices that would be predictive of basicity and ring strain.

The studies of Scrocco and Tomasi^{3,4}, Petrongolo⁵ and other investigators⁶ on the electrostatic molecular potential contour maps around molecules have demonstrated successful application of such contour maps to a wide variety of chemical problems (reactivity, structure, scattering and energetics of organic, inorganic and biological systems).

Our previous ab-initio quantum chemical calculations on morphine (an N-methyl narcotic agonist) and on nalorphine (an N-allyl narcotic antagonist-antagonist)⁷ had shown that while the N atom in both these compounds had the same charge (which we also verified experimentally by measuring their ESCA spectra⁸) morphine and nalorphine had very different pK_a's and also different ¹⁵N NMR shifts.⁹ The electrostatic molecular potential contour maps we generated from the ab-initio wave functions around the N atoms in morphine and nalorphine¹⁰ showed that while the charge on the N atom was the same and the maps were similar in the N lone pair direction, the maps around the N atoms were quite different in other directions. Obviously, charge alone on an atom does not seem to be sufficiently sensitive to distinguish different degrees of basicity, especially for closely related molecules. However, the use of electrostatic molecular potential contour

maps did hold promise of being a sensitive criterion for basicity. Comparisons of the sizes of the negative regions of the maps around the O atom in the ring should be indicative of the relative basicities of these exotic energetic cyclic ether monomers. The 3- and 4- member rings are the ones of choice for the experimental program. To this end we have carried out ab-initio MODPOT/VRDDO/MERGE calculations on oxetane, 3-fluoro-3-nitrooxetane and 3,3-dinitrooxetane (which were of first interest experimentally) and generated the electrostatic molecular potential maps around the molecules. Maps were also generated around 3-azidooxetane (of next interest experimentally) and around the complex of BF_3 catalyst attacking 3-azidooxetane. The results and interpretations of these studies are reported here.

II. Computational Details

The computations were carried out with our recent ab-initio programs^{11,12} that also incorporate several desirable options¹³⁻¹⁵: ab-initio effective core model potentials (MODPOT)¹⁶, which enable one to treat the valence electrons only explicitly, yet accurately; a charge-conserving integral prescreening evaluation¹⁷ (which we named VRDDO-variable retention of diatomic differential overlap¹³) especially effective for spatially extended molecules; and an efficient MERGE technique to reuse integrals from common skeletal fragments^{14e}.

The ab-initio effective core model potential formalism used is the one introduced by Bonifacic and Huzinaga¹⁶. The model potential consists of a static local potential that simulates the effect of the Coulomb and the exchange of the atomic core electrons and a set of projection operators that prevent the collapse of the valence shell orbitals into the inner cores. Only the valence electrons are considered explicitly. In the molecular case they introduced a spherical static potential to replace the local potential.

Our previous experience had shown that ab-initio MODPOT/VRDDO results would agree to about three decimal places for valence orbital energies and population analyses and to better than three decimal places for isomer total energy difference and potential energy curves with those quantities calculated by completely ab-initio calculations using the same valence atomic basis set¹⁴. The MERGE technique enables considerable savings in computer time when one is studying a series of similar compounds of even medium size.

The definition of the electrostatic potential of a molecule is given by

$$V(r) = \sum_{\alpha}^{\text{nuclei}} Z_{\alpha} / |\vec{r}_{\alpha} - \vec{r}| - \int d\vec{r}_1 \rho(\vec{r}_1) / |\vec{r}_1 - \vec{r}|$$

where $\rho(\vec{r}_1)$ is the electron distribution derived from the molecular wave function and Z_{α} are the nuclear charges. The first order interaction energy between the molecular charge distribution and a point charge distribution is

$$W = \sum_i q(\vec{r}_i) V(\vec{r}_i)$$

Such an expression has previously been used for comparative purposes.

III. Results and Discussion

Ab-initio MODPOT/VRDDO and ab-initio MODPOT/VRDDO/MERGE calculations were carried out for oxetane, 3-fluoro-3-nitrooxetane and 3,3-dinitroxetane (Figure 1), the geometries were optimized and electrostatic molecular potential maps were generated around the molecules in three directions: i) parallel to the mean molecular plane (xz); ii) parallel to the (xy) plane and iii) parallel to the (yz) plane. While the potentials were calculated for a 1000 points per plane for each of several dozen planes around the molecule we have only shown the maps of two of the most illustrative. Also on these maps the contours were drawn down to the -20 kcal contour (rather than include the more negative contours) so as not to clutter the maps. By focussing on the -20 kcal contour and watching the size of that contour it is illustrative of the relative difference in basicities. The results for

- (a) Oxetane (Figures 2a and b)
- (b) 3-Fluoro-3-nitrooxetane (Figures 3a and b)
- (c) 3,3-Dinitroxetane (Figures 4a and b)

indicate quite clearly that oxetane is the most basic, 3-fluoro-3-nitrooxetane is next and 3,3-dinitroxetane is the least basic. The ring strains are not expected to differ nearly as drastically in these molecules of similar ring size as do the basicities. We are currently developing theoretical procedures for calculating or estimating relative ring strains in these cyclic ethers. Thus, in response to question 1), it would be expected that oxetane would polymerize more easily than fluoronitroxetane and more easily than dinitroxetane. Our calculations were carried out prior to the experiments to polymerize fluoronitroxetane and dinitroxetane. Very recent experimental results validate our predictions¹⁸.

It was already known from the previous Japanese work that oxetane would polymerize with a Lewis acid catalyst. In the experimental work carried out in the overall ONR project 3-fluoro-3-nitrooxetane was synthesized and it undergoes cationic polymerization with a Lewis acid catalyst. 3,3-Dinitrooxetane was also synthesized, however its basicity is so diminished that it is extremely difficult to polymerize. The polymerization of 3,3-dinitrooxetane cannot be initiated in the conventional way with a Lewis acid, no matter how strong the Lewis acid.

We are currently also carrying out similar calculations to generate electrostatic molecular potential contour maps around a variety of other exotically energetically substituted oxetanes. These maps are sufficient to indicate the propensity of these oxetanes to undergo initiation for cationic polymerization. If the maps indicate a basicity of the substituted oxetane at least as great as that of 3-fluoro-3-nitrooxetane the monomer will undergo cationic polymerization. If the map indicates the basicity of the monomer is no greater than that of 3,3-dinitrooxetane, the monomer will not undergo initiation for cationic polymerization. This theoretical screening technique provides a valuable adjunct to the overall experimental program since theoretical calculations can be done prior to synthesis of the monomer. Many of these monomers are very difficult to synthesize and would not be synthesized if there were even reasonable indication that they would not undergo initiation of cationic polymerization.

These electrostatic molecular potential contour maps can also be used to help answer question 4) as to good candidate partners for co-polymerization. We hypothesized that since the rate of polymerization is very dependent on the basicity of the cyclic ethers, for good co-polymerization the copolymer molecules should have reasonably similar

basicities (as well as ring strains), because if one compound were much more basic than the other, it would self-polymerize so fast that it would not have much tendency to copolymerize. Such copolymers are especially valuable in the cases where the polymers formed from a single monomer are too brittle indicating too great a degree of structural regularity (such as for polymers of 3-fluoro-3-nitrooxetane¹⁸).

To shed insight on questions 2) and 3) we are also carrying out ab-initio MODPOT/VRDDO and ab-initio MODPOT/VRDDO/MERGE calculations on BF_3 approaching various series of substituted cyclic ethers and generating the electrostatic molecular potential contour maps. These results indicate the charge redistribution and changes in the maps as the reactants approach.

- (a) 3-azidooxetane (Figures 5 and 6)
- (b) 3-azidooxetane- BF_3 complex
B-O distance 5.0 Å (Figures 6a and b)
- (c) 3-azidooxetane- BF_3 complex
B-O distance 2.5 Å (Figures 7a and b)

Similar calculations are now being carried out for attack of H^+ on the substituted cyclic ethers since there has been speculation by experimental polymer chemists that perhaps it is the attack of H^+ (formed from a Lewis acid- H_2O complex) that triggers the polymerization¹⁹. However, experimentally it has been observed that different Lewis acid catalysts have different effects on polymerization of the same monomer. For example, it is possible to polymerize certain of these energetic monomers with PF_5 but not with BF_3 ¹⁹. This would seem to indicate that a catalyst-monomer complex might still be important. We have suggested several experiments that could help clarify the picture. First, to measure the

differing amounts of H^+ formed by various Lewis-acid catalysts in the polymerization solvent mixture (without any monomer as well as with monomers) to see if the amount of H^+ formed could explain the difference in propensity of a monomer to polymerize with different Lewis-acid catalysts. Second, to add various amounts of H^+ to solutions of monomer plus ineffective Lewis-acid catalyst to see if the extra H^+ could trigger the reaction. Third, to add various amounts of H^+ to solutions of monomer plus effective Lewis-acid catalysts to see if the rate or character of the polymerizations are affected.

IV. ACKNOWLEDGEMENTS

Our research on energetic materials and on new theoretical techniques for such energetic materials is supported by the Office of Naval Research, Materials Sciences Division, Power Programs Branch, under contract N00014-80-C-003 to The Johns Hopkins University.

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LIST OF FIGURE CAPTIONS

Figure 1. Sketches: Oxetane, 3-Fluoro-3-nitrooxetane, 3,3-Dinitrooxetane and 3-Azidooxetane

Figure 2a. Oxetane - Electrostatic Molecular Potential Contour Map, Parallel to the Mean Molecular Plane xz (In Plane)

b. Oxetane - Electrostatic Molecular Potential Contour Map, Parallel to the xy Plane (Through the O Atom)

Figure 3a. 3-Fluoro-3-nitrooxetane - Electrostatic Molecular Potential Contour Map, Parallel to the Mean Molecular Plane xz (In Plane)

b. 3-Fluoro-3-nitrooxetane - Electrostatic Molecular Potential Contour Map, Parallel to the xy Plane (Through the O Atom)

Figure 4a. 3,3-Dinitrooxetane - Electrostatic Molecular Potential Contour Map, Parallel to the Mean Molecular Plane xz (In Plane)

b. 3,3-Dinitrooxetane - Electrostatic Molecular Potential Contour Map, Parallel to the xy Plane (Through the O Atom)

Figure 5a. 3-Azidooxetane - Electrostatic Molecular Potential Contour Map, Parallel to the Mean Molecular Plane xz (In Plane)

b. 3-Azidooxetane - Electrostatic Molecular Potential Contour Map, Parallel to the xy Plane (Through the O Atom)

Figure 6a. 3-Azidooxetane-BF₃ Complex, B-O Distance 5.0 Å - Electrostatic Molecular Potential Contour Map, Parallel to the Mean Molecular Plane xz (In Plane)

b. 3-Azidooxetane-BF₃ Complex, B-O Distance 5.0 Å - Electrostatic Molecular Potential Contour Map, Parallel to the xy Plane (Through the O Atom)

Figure 7a. 3-Azidooxetane-BF₃ Complex, B-O Distance 2.5 Å - Electrostatic Molecular Potential Contour Map, Parallel to the Mean Molecular Plane xz (In Plane)

b. 3-Azidooxetane-BF₃ Complex, B-O Distance 2.5 Å - Electrostatic Molecular Potential Contour Map, Parallel to the xy Plane (Through the O Atom)

FIGURE 1

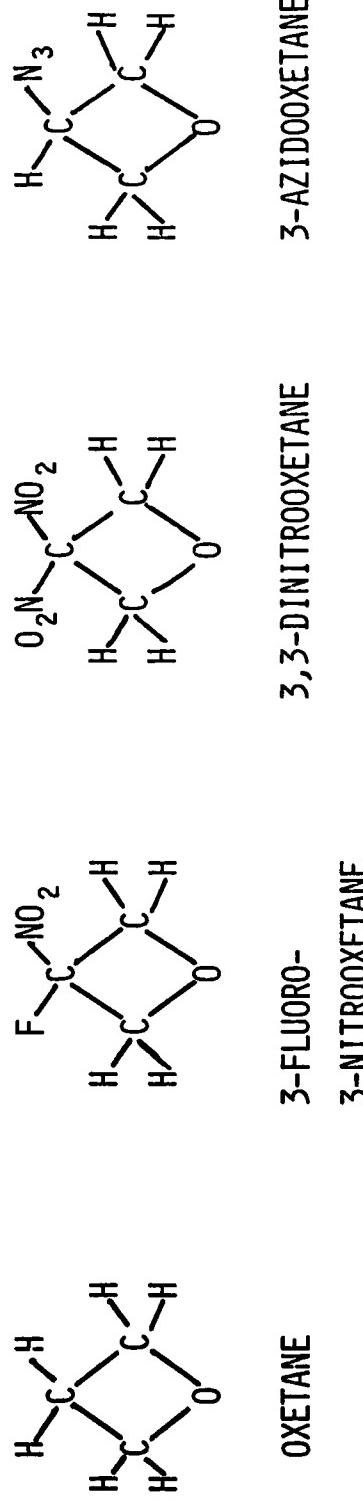


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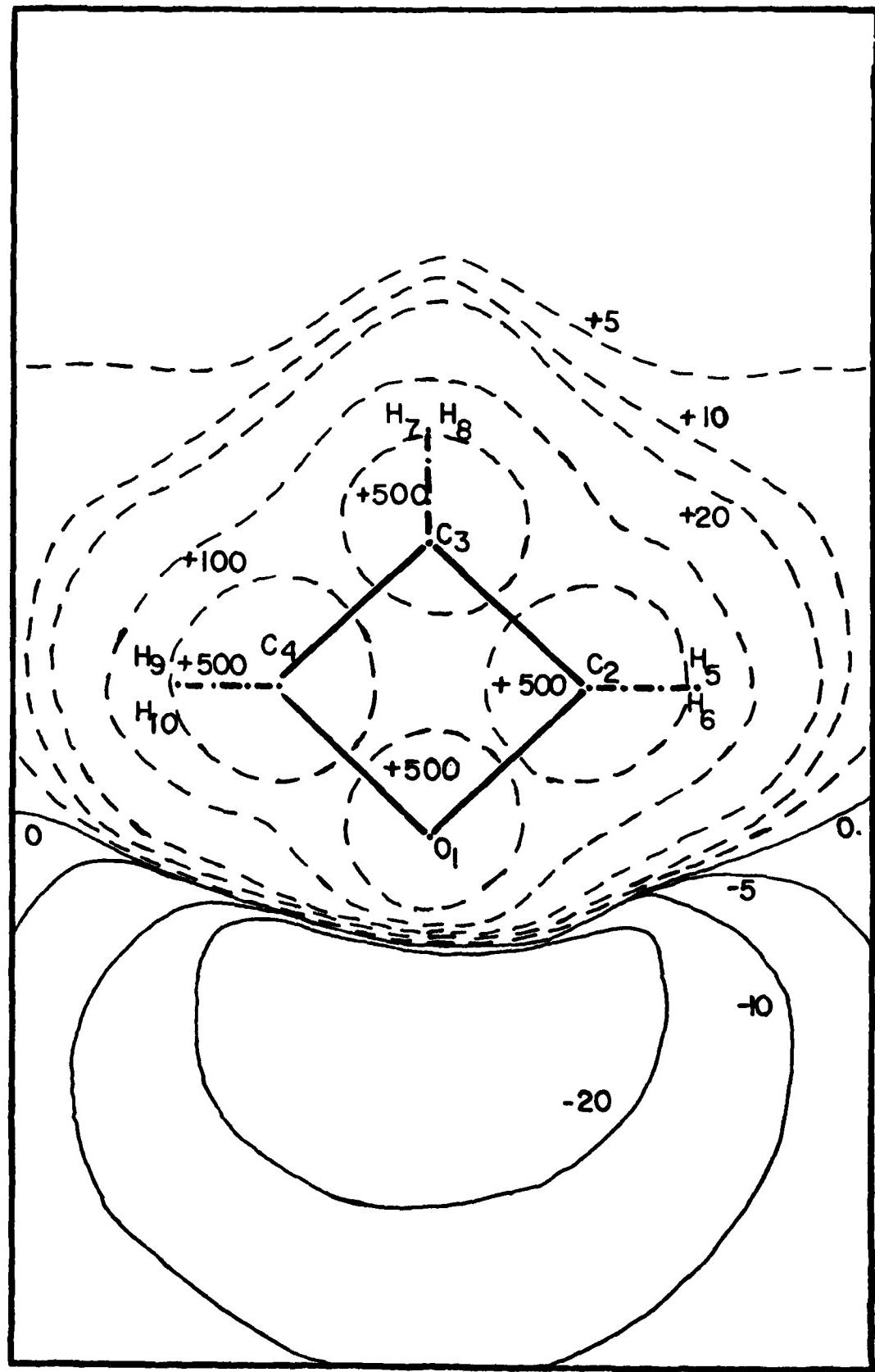


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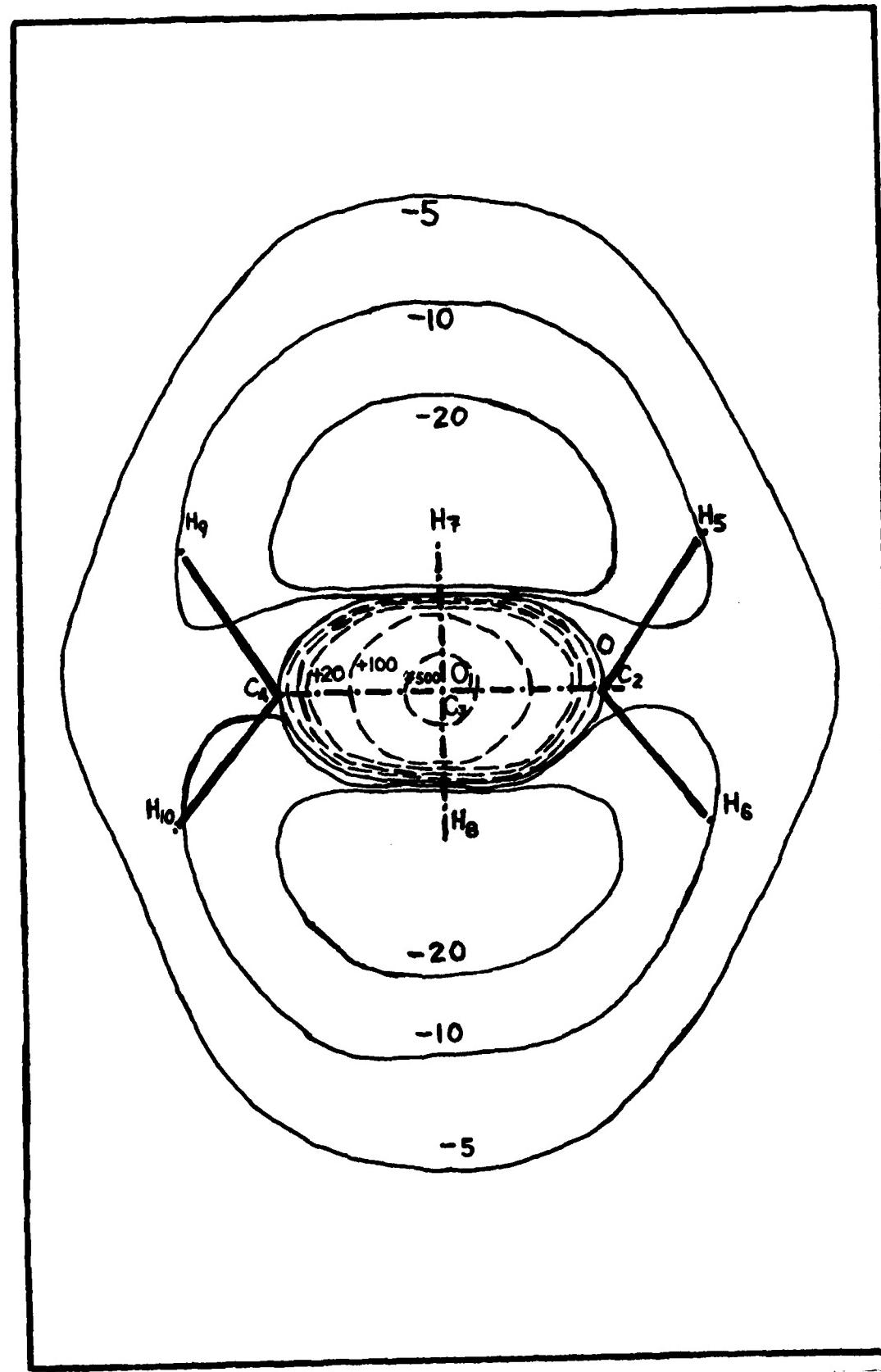


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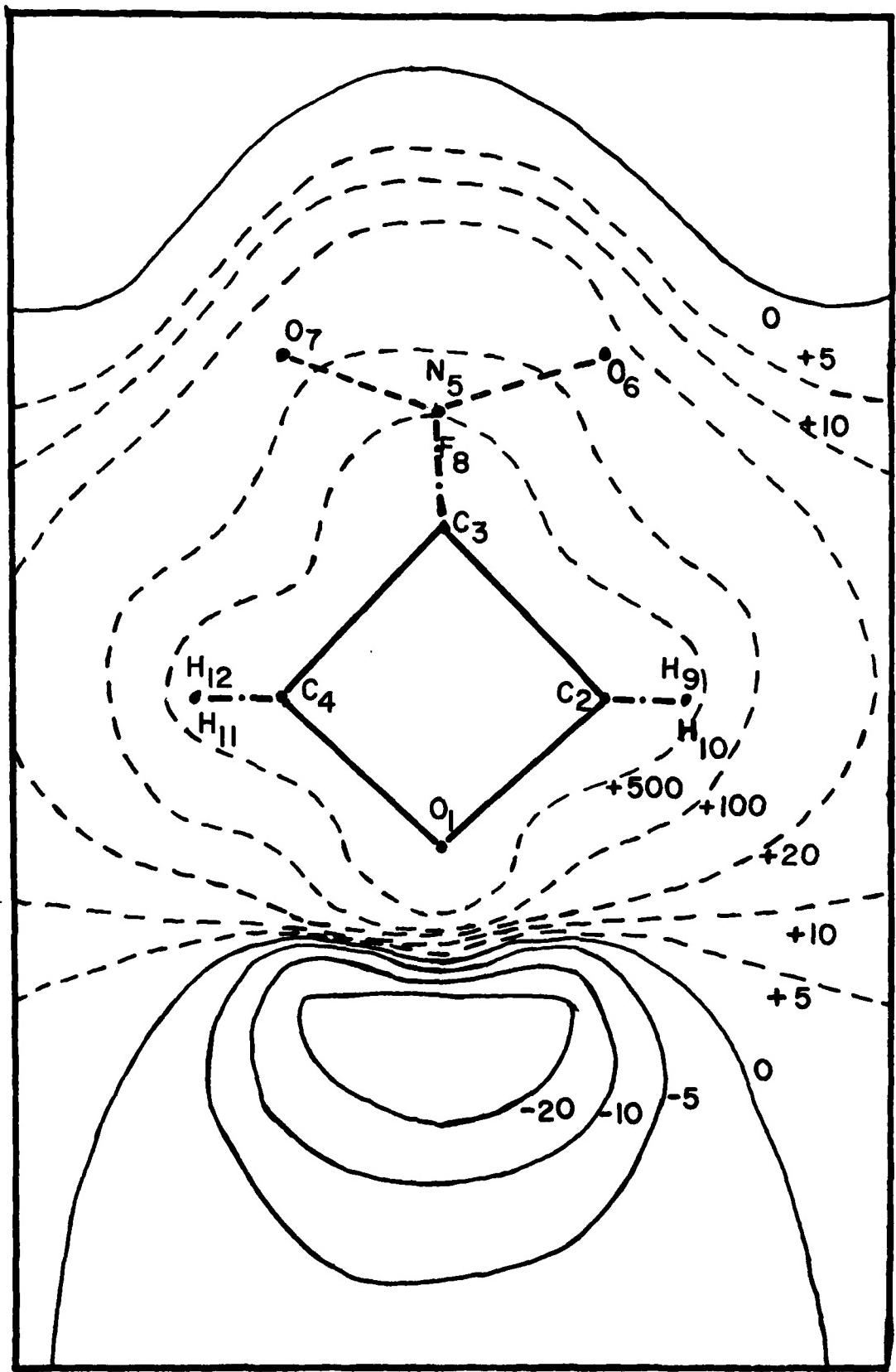


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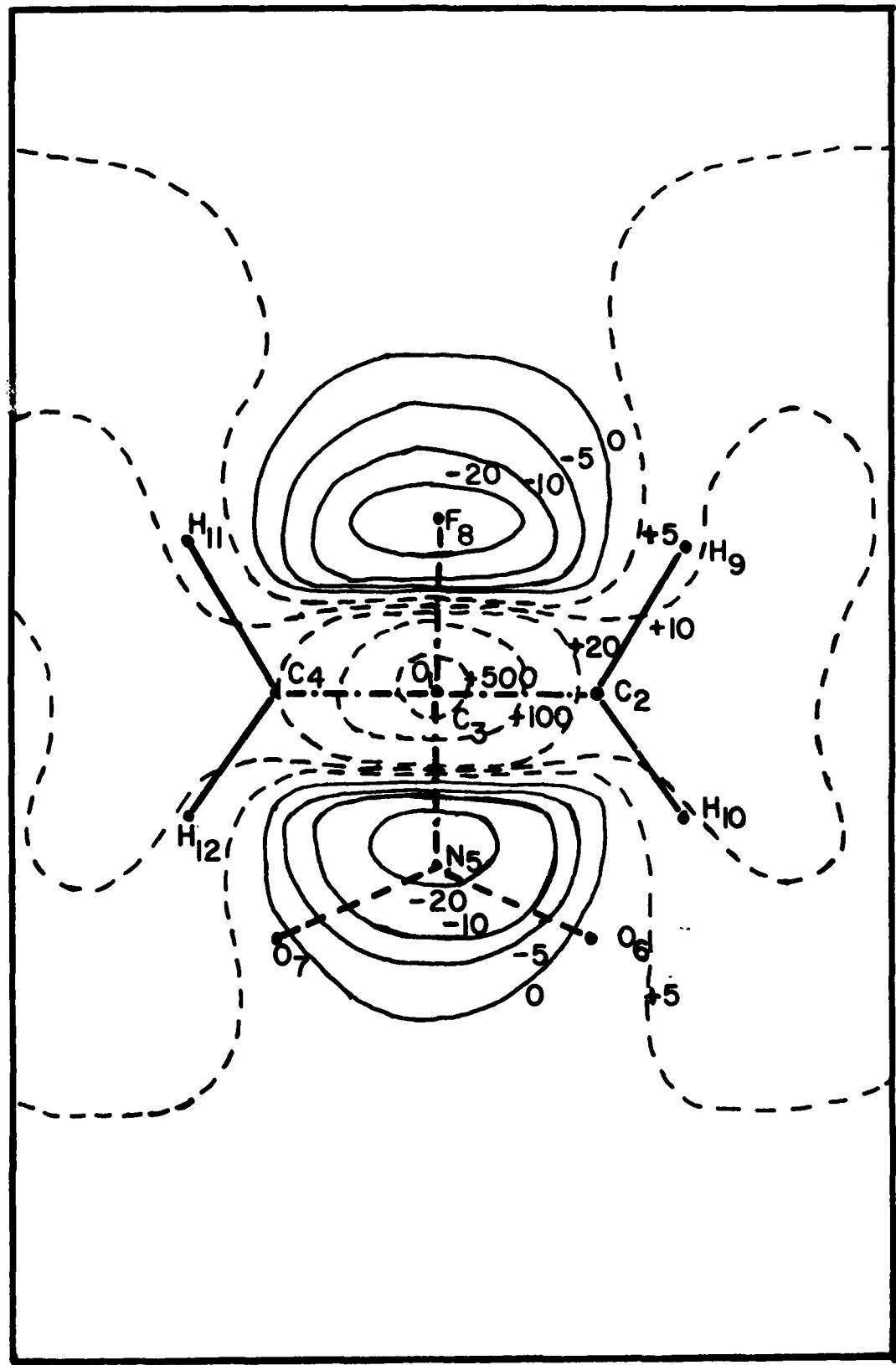


Figure 4a -

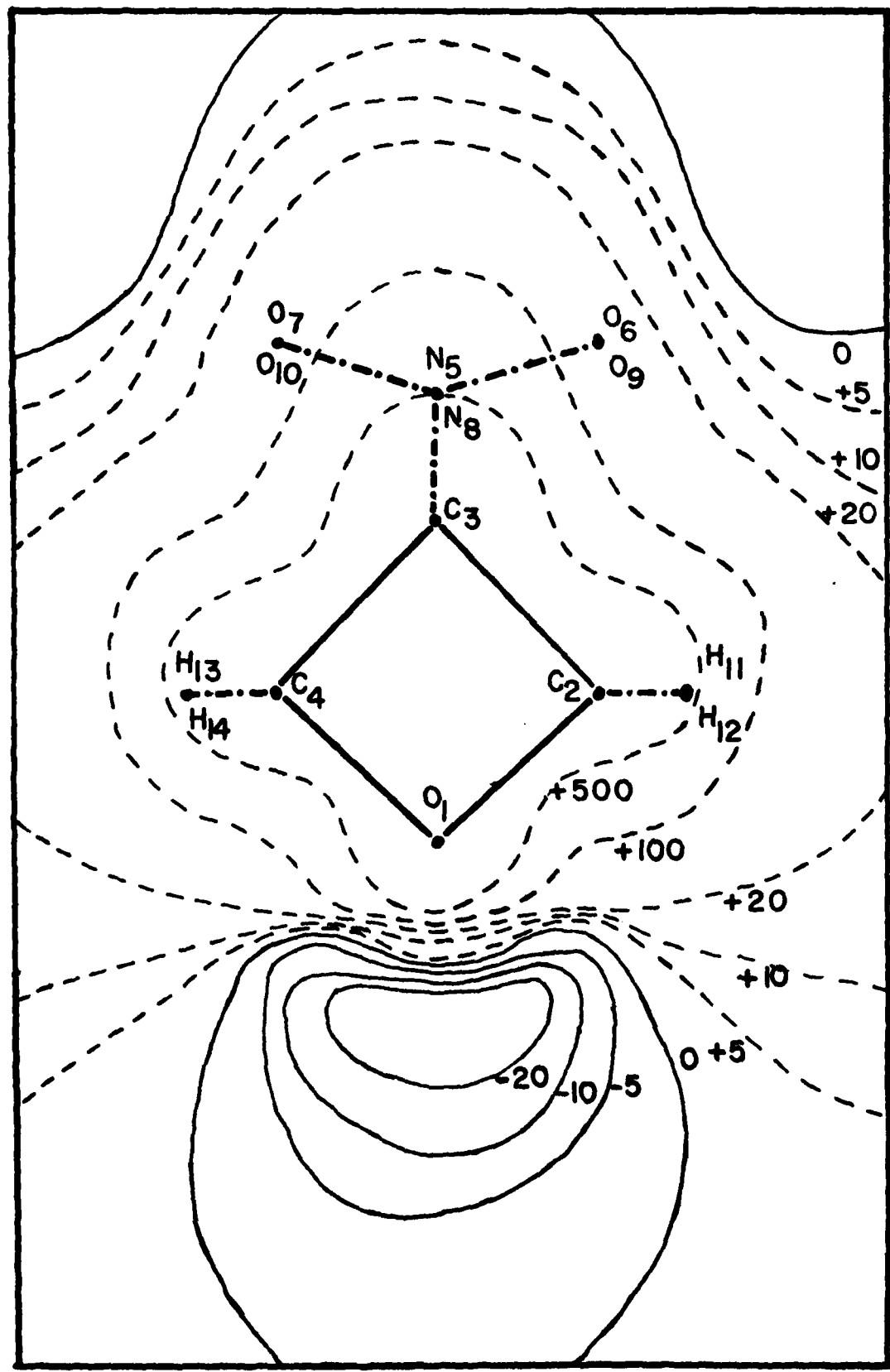


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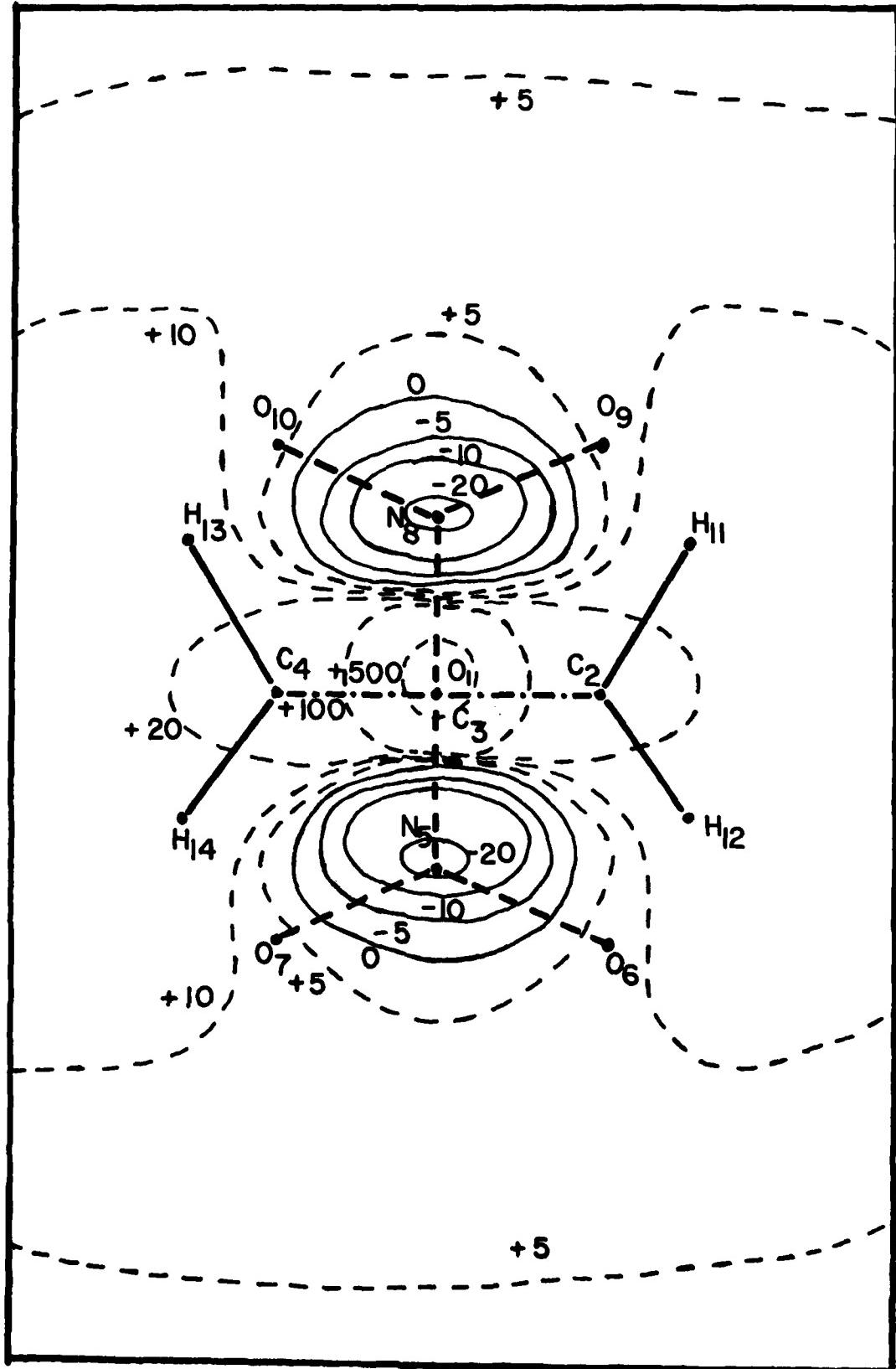


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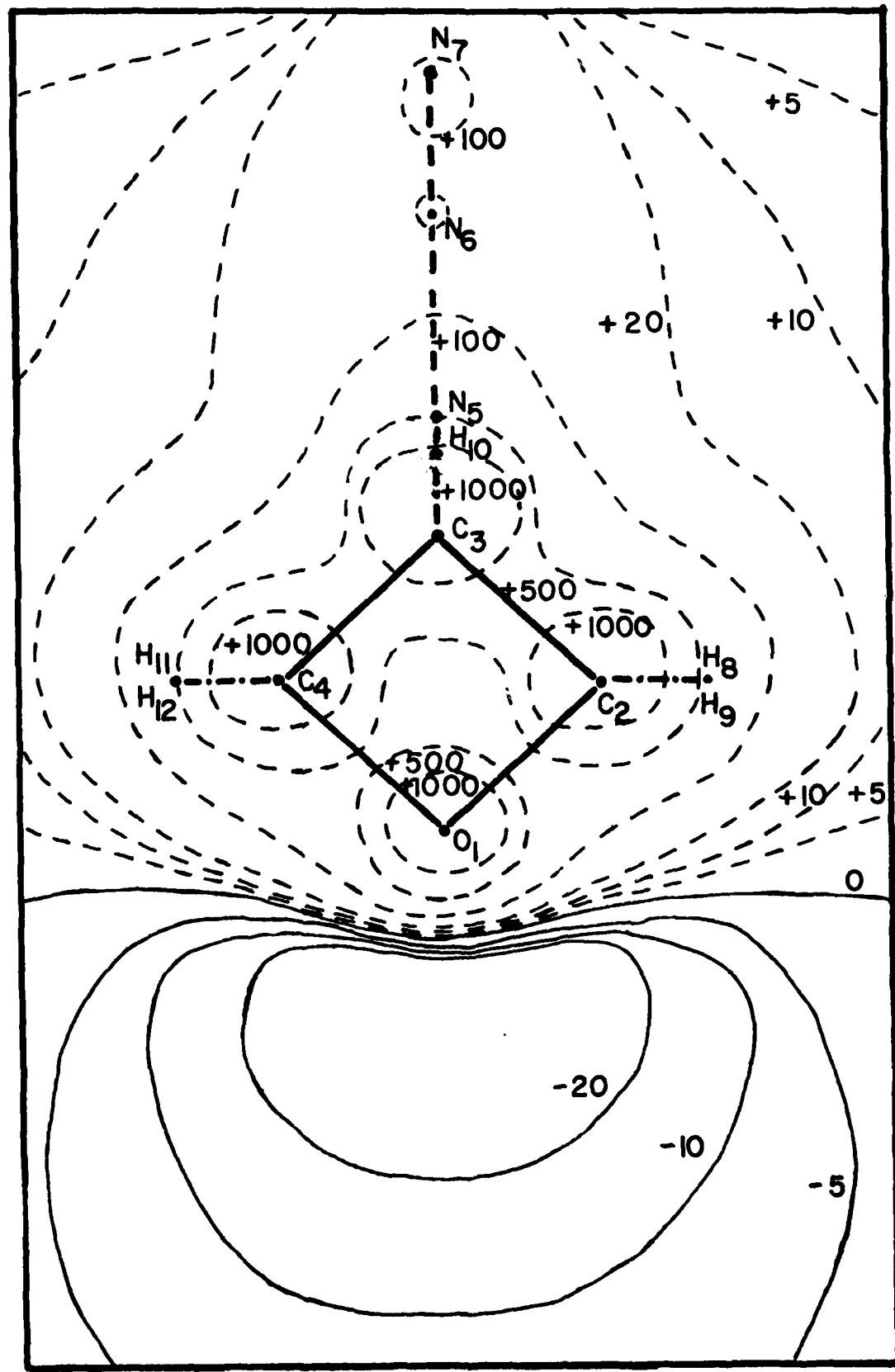


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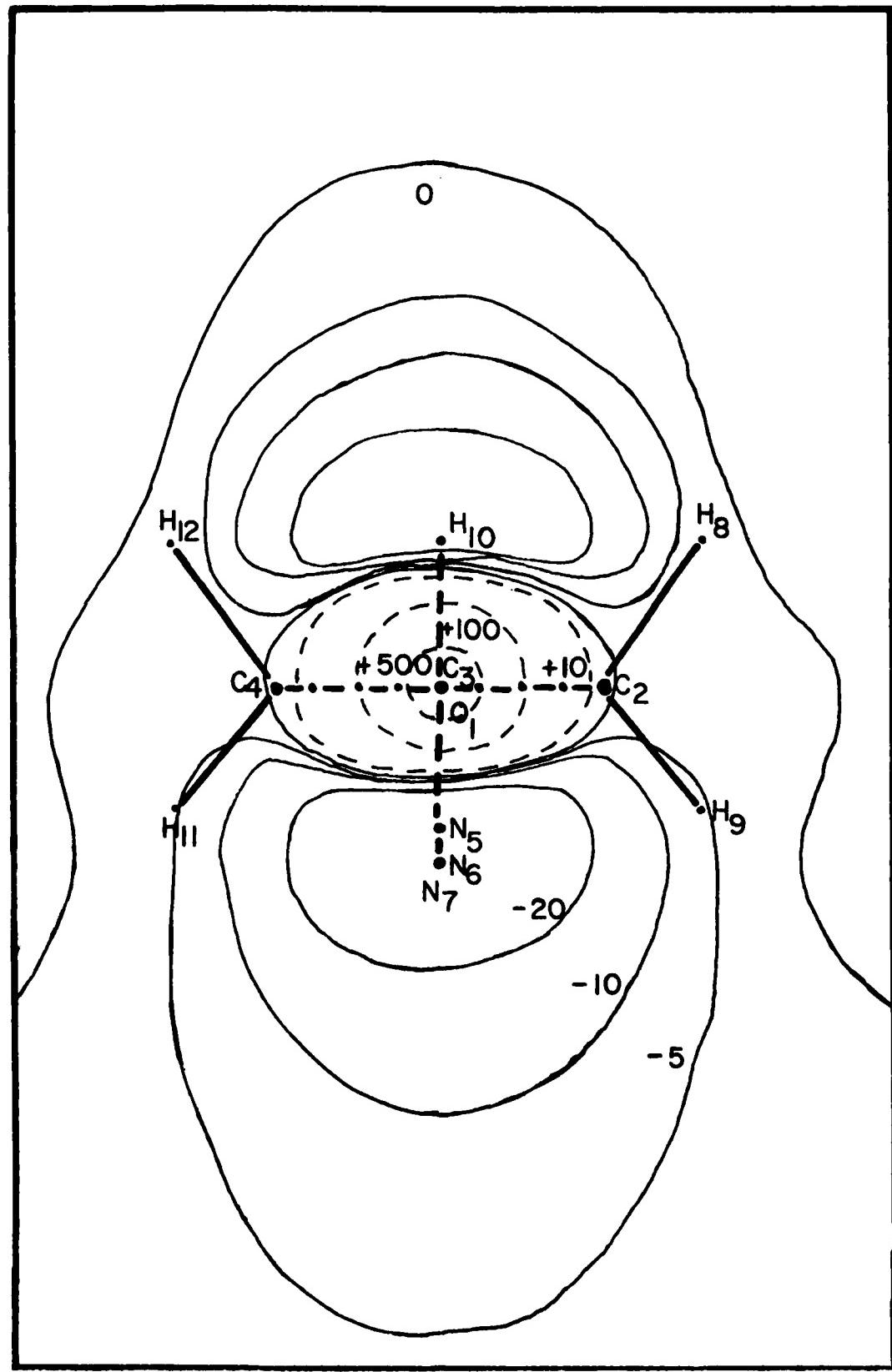


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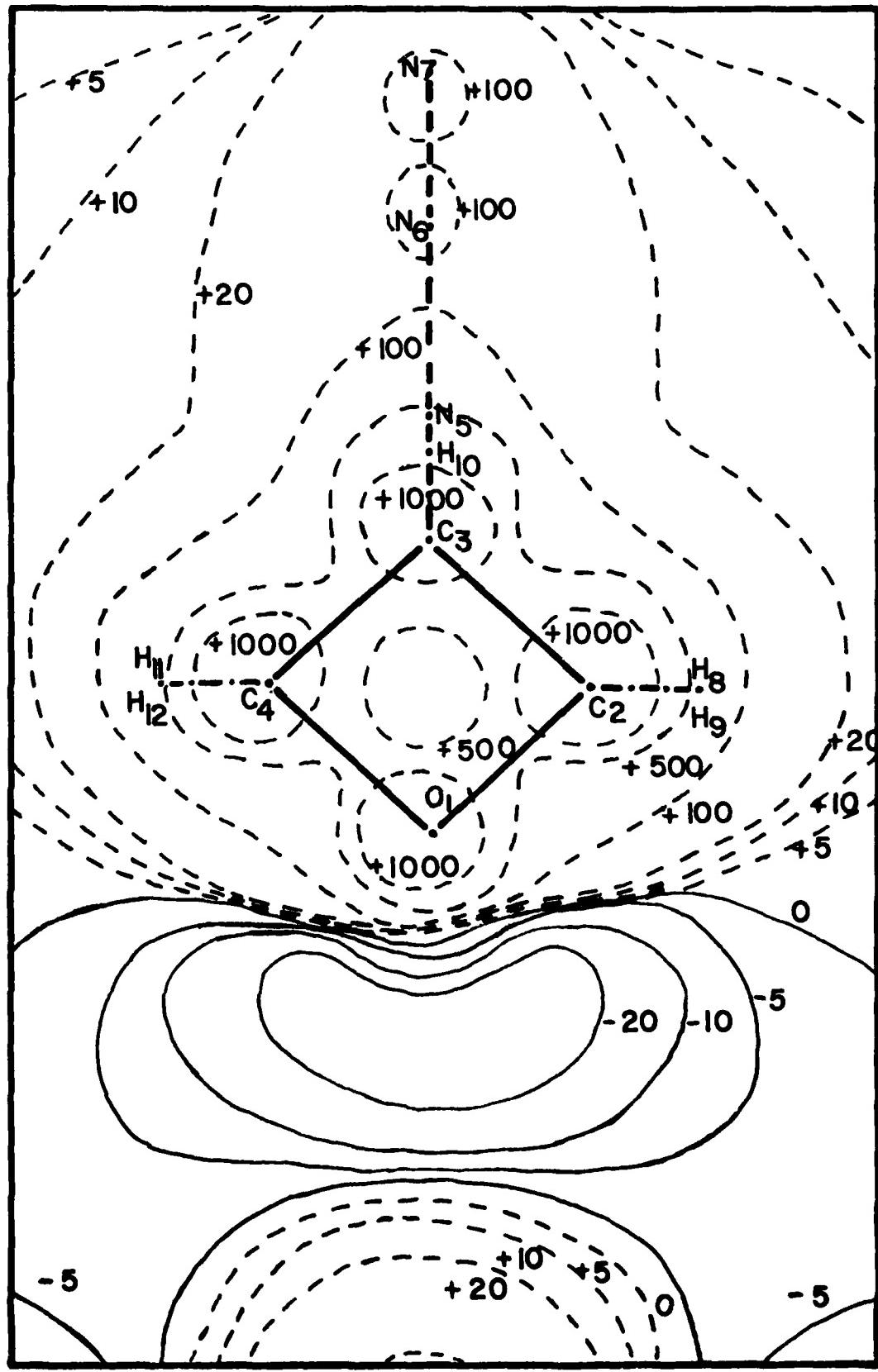


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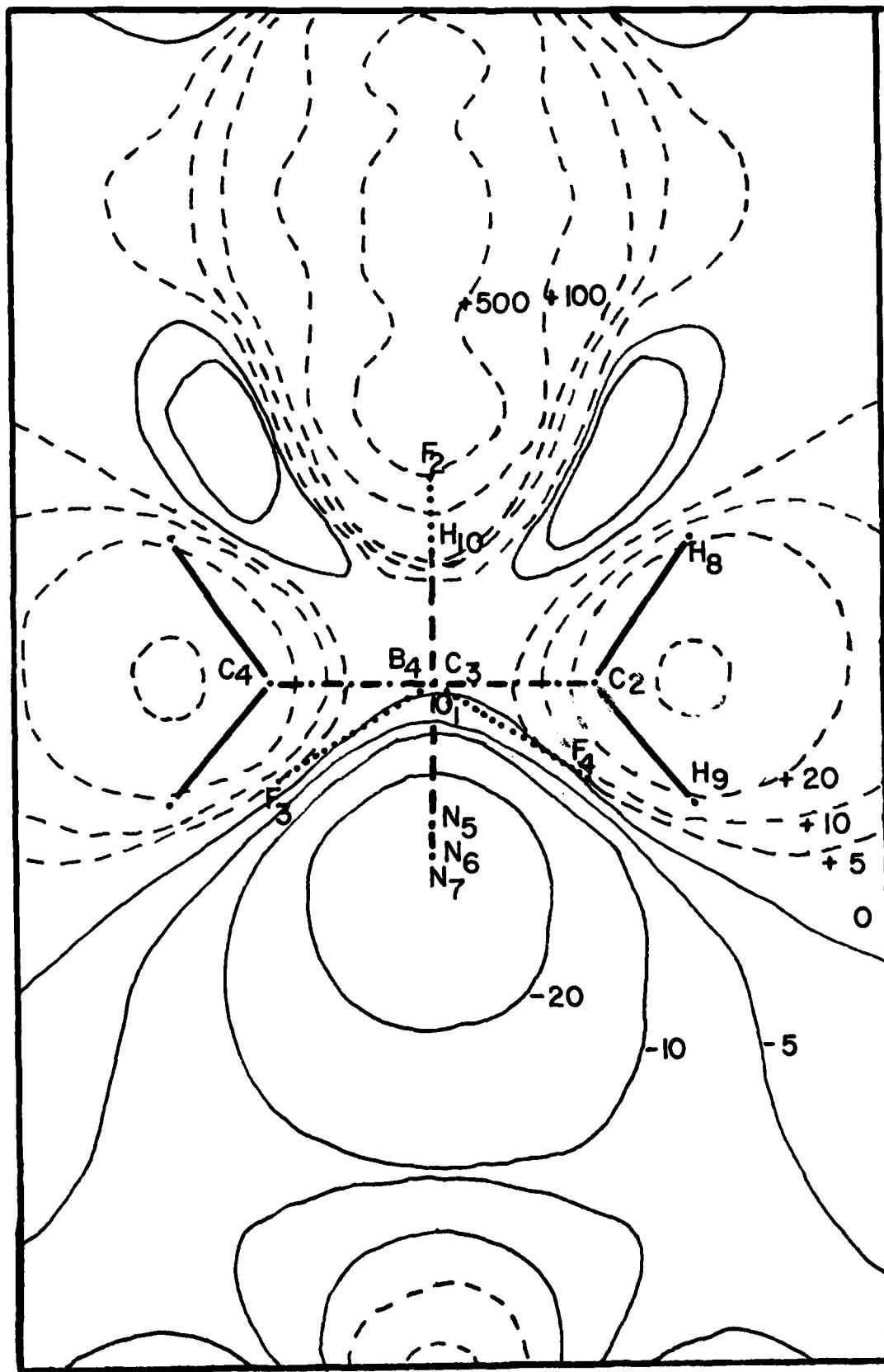


Figure 7a -

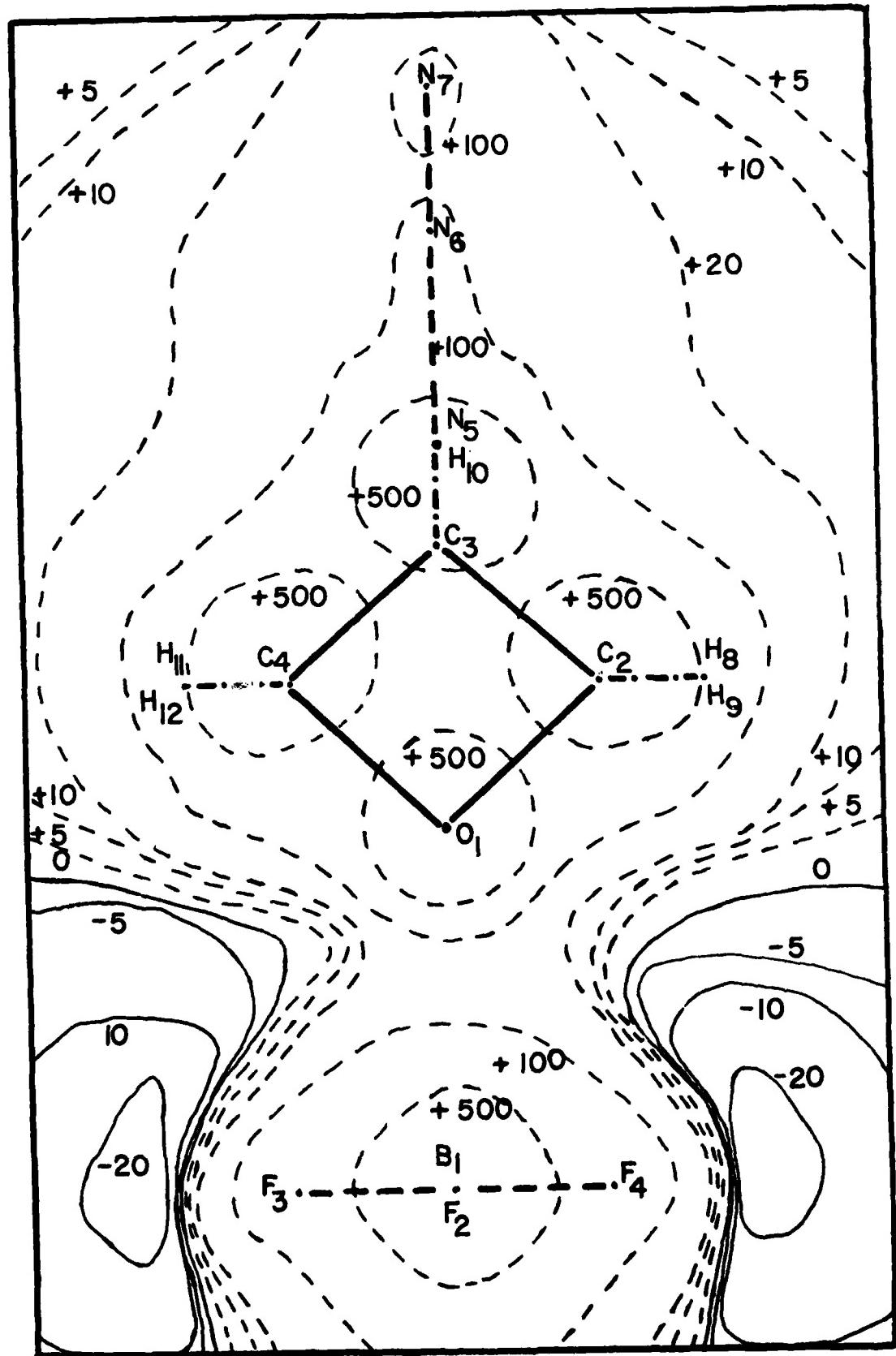
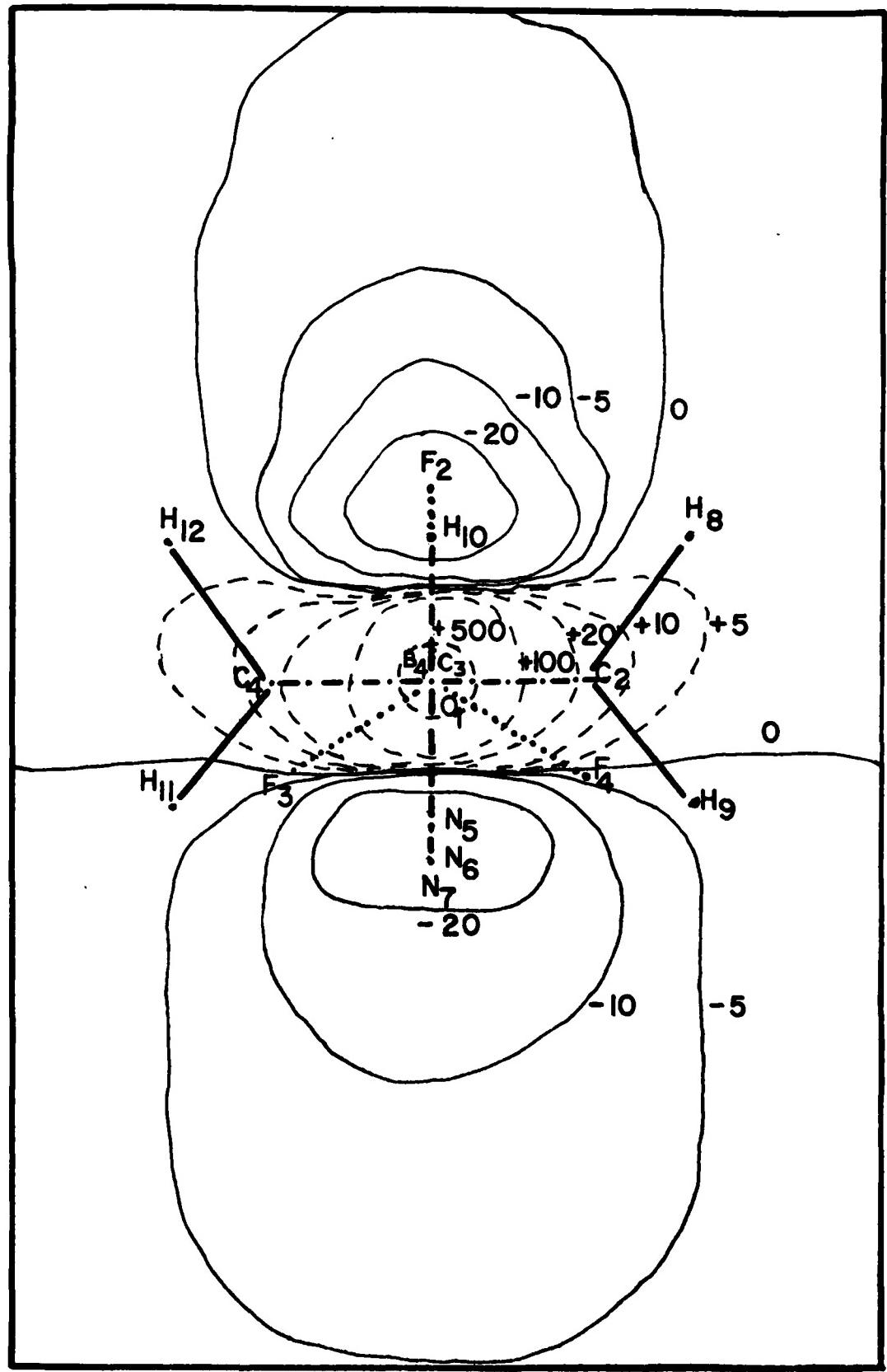


Figure 7b -



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